Behavior of molybdenum in pyrochemical reprocessing: A spectroscopic study of the chlorination of molybdenum and its oxides in chloride melts

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Abstract

The high temperature reactions of molybdenum and its oxides with chlorine and hydrogen chloride in molten alkali metal chlorides were investigated between 400 and 700 °C. The melts studied were LiCl–KCl, NaCl–CsCl and NaCl–KCl and the reactions were followed by in situ electronic absorption spectroscopy measurements. In these melts Mo reacts with Cl_2 and initially produces $MoCl_6^{2-}$ and then a mixture of Mo(III) and Mo(V) chlorocomplexes, the final proportion depending on the reaction conditions. The Mo(V) content can be removed as $MoCl_5$ from the melt under vacuum or be reduced to Mo(III) by Mo metal. The reaction of Mo when HCl gas is bubbled into alkali chloride melts yields only $MoCl_6^{3-}$. MoO_2 reacts in these melts with chlorine to form soluble $MoOCl_5^{2-}$ and volatile MoO_2Cl_2. MoO_3 is soluble in chloride melts and then decomposes into the oxychloride MoO_2Cl_2, which sublimes or can be sparged from the melt, and molybdate. Pyrochemical reprocessing can thus be employed for molybdenum since, after various intermediates, the end-products are chloride melts containing chloro and oxychloro anions of molybdenum plus molybdate, and volatile chlorides and oxychlorides that can be readily separated off. The reactions were fastest in the NaCl–KCl melt. The X-ray diffraction pattern of MoO_2Cl_2 is reported for the first time.
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1. Introduction

The chemical behavior of fission products in the reprocessing of oxide or metal fuels is an important topic for the nuclear fuel industry. Many fission products are generated during reactor operation, with typical distributions depending on the neutron energy and the respective fissile nuclide. Current commercial reprocessing is carried out using solvent extraction technology (Purex process) [1]. One prospective alternative for treating spent fuels is the pyrochemical process, and this involves using chloride melts, normally LiCl–KCl or NaCl–CsCl eutectic or the NaCl–KCl equimolar mixture. The renewed interest in this topic at this time arises in part from the increasing need to deal with spent oxide fuels.

One possible head-end of the pyrochemical process involves dissolution of spent ceramic fuels by chlorination in a molten salt bath. Reactions of transition metals and their oxides with chlorine in molten salts can be studied in situ using high temperature spectroscopy.

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This can provide important information concerning the behavior and speciation of the elements of interest. Solutions of metal ions with partially filled d- or f-orbitals exhibit characteristic absorption peaks in the uv-visible region due to d–d or f–f transitions, respectively. The intensity of such peaks is directly proportional to the concentration of the metal species in the melt. Consequently, it is possible to monitor the progress of a reaction upon measuring the electronic absorption spectra of the melts. We have recently investigated the behavior of technetium (another important fission product) during the high temperature molten salt chlorination process [2], using this approach.

Molybdenum is one of the major fission products, and stable ^{95}Mo, ^{97}Mo, ^{98}Mo and ^{100}Mo isotopes are all produced in high yields [3]. There is only one radioactive molybdenum isotope produced, ^{99}Mo, but this has a short half-life of 2.75 days. Spent fuel arriving for reprocessing from thermal reactors contains 4–8 kg of molybdenum per tonne [4].

Molybdenum in spent ceramic UO_2-based fuels forms both metallic and oxide precipitates [5,6]. There are continuous transitions between these two forms due to solubility limits of the fission products and an increase in the chemical potential of oxygen for the total system during burn-up and, consequently, a change in the chemical state.

Molybdenum metal is normally present as a constituent of Mo–Tc–Ru–Rh–Pd inclusions [5–8]. The composition of these metallic alloys varies considerably and depends on the fission yield; the initial O/(U + Pu) ratio of the fuel (i.e., the oxygen potential); the temperature gradients in the fuel rod; and the burn-up [5]. As the

oxygen potential of the Mo/MoO_2 equilibrium is similar to slightly hypostoichiometric uranium–plutonium oxide fuel, the metallic molybdenum concentration in the alloys decreases continuously by oxidation of this element during irradiation, due to an increase in the oxygen potential of the fuel with burn-up. This increase arises because the oxygen, liberated from uranium and plutonium oxides by their fission, cannot be completely consumed by the generated fission products [5].

$$[Mo]_{alloy} + (O_2) \rightarrow [MoO_2]_{oxide\ phase} \qquad (1)$$
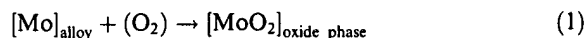
Since the solubility of MoO_2 in UO_2 and $(U-Pu)O_2$ is negligibly small, MoO_2 is considered as an independent oxide isolated from the dioxide lattice [9]. Molybdenum is also capable of migrating to cooler regions of the fuel-pin by means of gaseous molecules, e.g., MoO_3 [5]. Apart from molybdenum metal and oxides, there is some indication that anionic oxide species are formed [9], and these include MoO_3^{2-} and MoO_4^{2-}.

The available information on the spectra of molybdenum species in molten salts is limited, Table 1. Scheffler et al. [10] reported the spectra of Mo(III) and Mo(IV) chlorocomplexes in $AlCl_3$-1-ethyl-3-methylimidazolium (emim) chloride at room temperature. Later Carlin and Osteryoung [11] and Barnard et al. [12] studied molybdenum(II) and (III) chloride dimers in the same room temperature system but there are reports of such dimers in high temperature studies. Available high-temperature spectroscopy studies are limited to Aleksandrov et al. [13] on the spectra of Mo(III) solutions obtained by anodic dissolution of Mo metal in CsCl, NaCl–CsCl and NaCl–KCl melts; and Gabriel et al. [14]

Table 1
Electronic absorption spectroscopy data for $[MoCl_6]^{x-}$

Species	Solvent	T, °C	Peak maxima, nm $z(\varepsilon, dm^3\ mol^{-1}\ cm^{-1})^a$	Ref.
$[MoCl_6]^-$	NaCl–CsCl	502	Intense band <450	[13]
$[MoCl_6]^-$	KCl	Quenched melt	415[b]	[15]
$[MoCl_6]^{2-}$	44.4/55.6 mol.% AlCl₃–MEIC	25	366 (4400), 391 (4500), 451[b]	[10]
$[MoCl_6]^{2-}$	LiCl–KCl	450	380, 470	This work
$[MoCl_6]^{3-}$	44.4/55.6 mol.% AlCl₃–MEIC	25	439 (36), 544 (30), 685 (1.6)	[10]
$[MoCl_6]^{3-}$	CsCl	692	446, 592, 699	[13]
$[MoCl_6]^{3-}$	NaCl–CsCl	515	444, 575, 699	[13]
$[MoCl_6]^{3-}$	NaCl–CsCl	695	444, 599, 699	[13]
$[MoCl_6]^{3-}$	NaCl–KCl	695	442, 595, 699	[13]
$[MoCl_6]^{3-}$	LiCl–KCl	400	425 (44), 552 (29), 685[b] (5.9)	[14]
$[MoCl_6]^{3-}$	LiCl–KCl	400	340 (86), 420 (64), 550 (39), 685[b] (13)	[14]
$[MoCl_6]^{3-}$	NaCl–CsCl	600	570, 685[b]	This work
$[MoCl_6]^{3-}$	NaCl–KCl	700	436, 583, 684	This work

^{a} ε, molar absorbance.
^{b} Shoulder.

on the stability of molybdenum(III) solutions in LiCl–KCl eutectic. In both these studies the authors observed disproportionation of Mo(III) at high temperature, yielding Mo(V) and an insoluble fraction, attributed to molybdenum metal. Horner and Tyree [15] prepared $MoCl_6^-$ species by fusing KCl and $MoCl_5$ but measured the spectra only of quenched melts. We here describe our spectroscopic studies on the chlorination (and hence oxidation) of molybdenum metal and the oxides MoO_2 and MoO_3 in LiCl–KCl, NaCl–KCl and NaCl–CsCl melts.

2. Experimental

Experiments were performed in three different melts, LiCl–KCl eutectic (41.5 mol.% KCl, mp 361 °C), NaCl–CsCl eutectic (64 mol.% CsCl, mp 490 °C) and NaCl–KCl equimolar mixture (mp 658 °C). NaCl–CsCl eutectic was prepared by fusing dried individual salts mixed in the required proportion, LiCl–KCl eutectic (Alfa) and the NaCl–KCl mixture (polarographic grade, Ubichem Limited) were used as received.

Spectra were recorded using a custom-built set-up based on an Ocean Optics SD2000 double channel computer-controlled fiber optic spectrophotometer. A deuterium-halogen light source, DH-2000, provided illumination between 210 and 1100 nm. Details of our procedure for recording spectra during the chlorination process are reported elsewhere [2]. Experiments were performed in a standard 1 cm optical silica cell, attached to a silica tube ($\approx$25 cm long) with two side-arms in the upper region. The cell was closed using a silicone rubber stopper through which a silica capillary tube was passed. Chlorine or HCl, as required, was introduced into the cell atmosphere or bubbled through the melt via this vertical silica tube (3 mm i.d.), which could be raised from or lowered to the bottom of the cell as required. One side-arm of the cell was connected to a vacuum/argon line. The other side-arm was connected to a concentrated sulfuric acid bubbler through which gases could exit. When required, the spectra were resolved into individual bands using Peak Fit™ (Jandel Scientific, version 4.1) software.

Chlorine and hydrogen chloride gases used as chlorinating agents were pre-dried by bubbling through the conc. sulfuric acid prior to use. Before recording the baseline spectra the melts were saturated with chlorine or hydrogen chloride to compensate for the absorbance caused by the significant solubilities of these gases in molten chlorides at the high temperatures employed. Commercially available molybdenum (powder and 1 mm dia wire, Goodfellows) and the molybdenum oxides MoO_2 and MoO_3 (Aldrich) were used. A unique advantage of fiber optic spectroscopy over conventional spectrophotometers is that the small diameter light beam

can be located both normal to the optical flat surface and anywhere over it so that any particles present in the liquid are out of the beam. This latter feature was employed when molybdenum metal powder or solid oxides were present.

The X-ray diffraction instrument used was a Phillips PW1710 diffractometer and infrared spectra were recorded on a (MIDAC) FTIR spectrometer.

3. Results and discussion

3.1. Reaction of molybdenum metal with chlorine

The reaction of transition metals with Cl_2 in molten chlorides is a convenient way of dissolving such metals. This method, however, often results in the formation of species having the metal in the highest stable oxidation state, e.g., forming $NbCl_6^-$ and $TaCl_6^-$ upon the chlorination of Nb and Ta, respectively [16,17]. It was therefore initially anticipated that the reaction with molybdenum would result in the oxidation of Mo(0) to one of the higher oxidation states, V or VI.

Experiments were first conducted in LiCl–KCl melt using molybdenum metal powder at 400 °C. Upon introducing chlorine into the atmosphere above the LiCl–KCl melt containing Mo powder, a very fast reaction took place and a dark red vapor appeared. The melt assumed a red color and the absorbance below 400 nm started to rise and after a few seconds exceeded four absorbance units, the spectrophotometer limit. Molybdenum species formed could not be identified from the color of the reaction product since $MoCl_3$ and $MoCl_4$ are red, $MoCl_5$ vapor is dark red (although the solid compound is green–black or blue–black), and $(MoCl_2)_3$, $MoCl_3$ and $MoCl_5$ can form red solutions. Molybdenum chloride species, containing Mo in various oxidation states, can in theory be distinguished by their electronic absorption spectra, Table 1.

By conducting the above experiment with a compact form of molybdenum (Mo wire) the reaction was slowed down and a spectrum obtained after 10 s of chlorination (at 450 °C) is shown in Fig. 1. The spectrum was resolved into individual bands. The absence of absorbance above 500 nm indicates that the melt did not contain $MoCl_6^{3-}$, which is well studied and has a peak around 550 nm (Table 1). The spectrum of Mo(VI), configuration d^0, will not have absorption d–d bands in the visible region (the existence of $MoCl_6$ is still disputed: it can possibly be formed under high Cl_2 pressure); Mo(V), d^1, will have only one band, in regular octahedral symmetry, corresponding to the $^2T_{2g} \rightarrow {}^2E_g$ transition in $MoCl_6^-$, with a maximum between 415–450 nm [13,15], Table 1. There is only one relevant example in the literature of the spectrum attributed to $MoCl_6^{2-}$, obtained by dissolving $MoCl_5$ in emim chloroaluminate room temperature
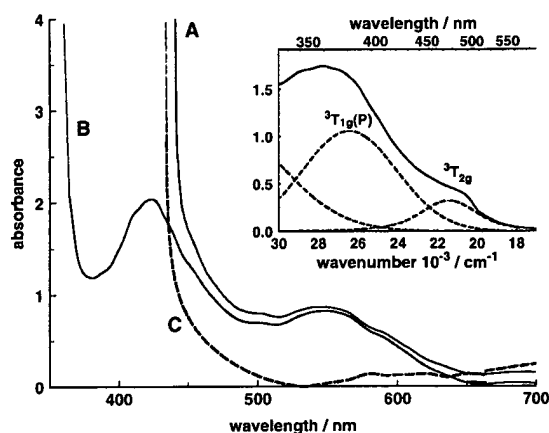
Fig. 1. A, spectrum of solution obtained by reacting Mo powder with Cl_2 in LiCl–KCl melt, 400 °C. B, after evacuating for 13 min (Mo(V) removed). C, spectrum resulting from reaction of a solution containing only $MoCl_6^{3-}$ with Cl_2: solution now contains mainly $MoCl_6^-$. Insert shows spectrum of $MoCl_6^{2-}$ recorded after passing Cl_2 for 10 s into LiCl–KCl eutectic melt at 450 °C containing Mo wire. The spectrum resolved into individual bands and transitions from the ground $^3T_{1g}(F)$ state are indicated.

melts [10], Table 1. The peaks attributed by Scheffler et al. [10] to $MoCl_6^{2-}$ do not correspond to the transitions that can be expected for d^2-configuration in octahedral symmetry and the symmetry of their complex must thus be distorted. Mo(II) species cannot be formed in high temperature melts under oxidizing conditions. Resolution of the spectrum in Fig. 1 into individual components revealed two bands, attributed to $^3T_{1g} \to ^3T_{2g}$ and $^3T_{1g} \to ^3T_{1g}(P)$ transitions in $MoCl_6^{2-}$ complex. Based on the energies of these transitions (Table 1) the following values of the main spectroscopic parameters were calculated, $Dq = 2240$ cm^{-1} and $B = 399$ cm^{-1}. This value of Dq, which depends on the metal oxidation state, is in excellent agreement with that of 2220 cm^{-1} reported by Horner and Tyree [15] for $MoCl_6^{2-}$. The high molar absorption coefficients reported for the molybdenum(IV) chlorocomplex [10] give further supporting evidence that the spectrum in Fig. 1 is due to the Mo(IV) species, because very small amounts of $MoCl_6^{2-}$ will produce high absorption values. However, it cannot be excluded that some $MoCl_6^-$ has also been formed. Molybdenum(IV) chloride is also one of the products of the reaction of molybdenum with chlorine [18]. Therefore, the reaction of molybdenum metal with chlorine in molten chlorides starts with the fast (within a few seconds) formation of the molybdenum(IV) chloro-species, viz.,

$$Mo + 2Cl_2 + 2Cl^- \to MoCl_6^{2-} \qquad (2)$$
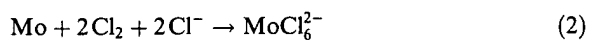
This process can also in principle proceed in two rapid stages:

$$Mo + 3/2Cl_2 + 3Cl^- \to MoCl_6^{3-} \qquad (3)$$

$$MoCl_6^{3-} + 1/2Cl_2 \to MoCl_6^{2-} + Cl^- \qquad (4)$$
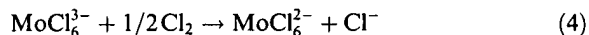
However, as was shown in [13] and as we found here, the oxidation of $MoCl_6^{3-}$ by chlorine results in the formation of $MoCl_6^-$.

Introducing chlorine into the atmosphere above a LiCl–KCl melt containing molybdenum powder at 400 °C results in the formation of a dark red melt and the absorbance below 500 nm increases rapidly. The spectrum recorded after passing Cl_2 above the melt for 12 min is presented in Fig. 1 (line A). Aiming to decrease the concentration of dissolved molybdenum by removing any volatile species, the flow of chlorine was stopped and the cell evacuated. The spectrum recorded after 13 min under vacuum is profile B in Fig. 1. It can be seen that the absorbance did not change much in the 500–600 nm range but decreased considerably below 500 nm and a previously masked peak around 420 nm appeared. The resulting profile, B, corresponds closely to the spectrum of $MoCl_6^{3-}$ reported by Scheffler et al. [10] at 25 °C, and by Aleksandrov et al. [13] and Gabriel et al. [14] in high temperature melts. During the evacuation the absorbance above 500 nm remained essentially unchanged but below 500 nm there was a considerable decrease. This indicates that spectrum A was a consequence of at least two molybdenum species present in the melt, one being $MoCl_6^{3-}$ and another, or the other, being a volatile species. Apart from the dissolved chlorine, molybdenum(V) chloride (b.p. 268 °C [19]) is the obvious candidate for the volatile component of the mixture, particularly since its only d–d transition can be expected at relatively high energies, similar to those of Nb(IV) [20] and Ta(IV) [21]. The spectra of solutions of $MoCl_6^-$ in the NaCl–CsCl melt [13] showed only the edge of a very intense band below 450 nm. This corresponds to the absorbance lost under vacuum and thus provides further evidence that the volatile species was the Mo(V) chloride:

$$MoCl_6^- \to MoCl_5 \uparrow + Cl^- \qquad (5)$$

When the system was returned to 1 atm pressure (Ar atmosphere) the spectrum changed back to A (in Figs. 1 and 2). At high temperatures in chloride melts Mo(III) disproportionates to Mo(V) and Mo metal [13,14]:

$$5MoCl_6^{3-} \to 3MoCl_6^- + 2Mo \qquad (6)$$

and the $MoCl_6^-$ formed and now remaining in the melt was responsible for the absorbance below 450 nm.

Bubbling chlorine (at a rate of about 40–60 bubbles per minute) through this red melt resulted in a series of rapid changes in the spectra, Fig. 2. The absorbance around 500–600 nm started to decrease and after about 10 min reached essentially zero at ≈530 nm. At the same
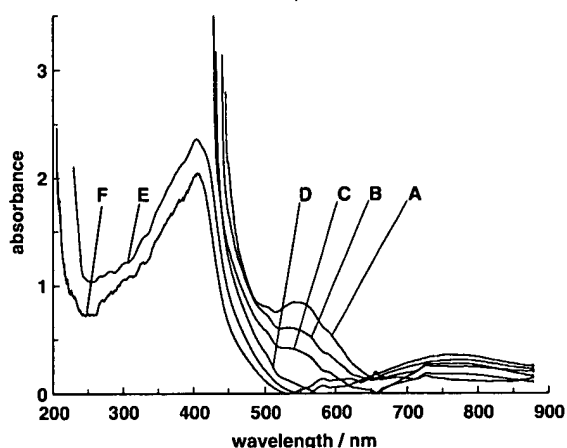
Fig. 2. Reaction of $MoCl_6^{3-}$ with Cl_2 in LiCl–KCl at 400 °C. Time of chlorination, min: A, 0; B, 1; C, 3; D, 5; E, 9 and F, 11.

time, the absorbance increased slightly at around 800 nm. In the uv-region, the absorbance also decreased and eventually a maximum was recorded just above 400 nm. By this time the melt had changed from red to pale yellow (or greenish-yellow). The color of the melt, together with the zero absorbance at 530 nm, indicated the loss of all trivalent $MoCl_6^{3-}$ from the melt.

During this stage of the experiment, gentle bubbling of chlorine through the melt had thus resulted in further oxidation of molybdenum from Mo(III) to Mo(V), and with no evidence for other oxidation states:

$$MoCl_6^{3-} + Cl_2 \rightarrow MoCl_6^- + 2Cl^- \tag{7}$$
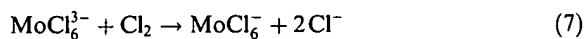
Previously Aleksandrov et al. [13] oxidized Mo(III) in a NaCl–CsCl melt by chlorine bubbling and then removed dissolved chlorine by sparging the melt with argon. They concluded that after this treatment molybdenum in the melt was oxidized to Mo(V) and the spectrum showed only an edge of a very intense absorption band below 450 nm. The reported spectrum [13] shows some weak absorbance in the visible region, but no comments thereon were made. This additional band could indicate some distortion of $MoCl_6^-$ from octahedral symmetry.

The final two spectra in Fig. 2 (recorded after 9 and 11 min of chlorination and oxidation of Mo(III)) exhibit a maximum at ≈400 nm and a broad low intensity band around 760 nm, agreeing with the spectra obtained by Aleksandrov et al. [13]. In the spectra of quenched KCl–$MoCl_5$ melts a band was reported with a maximum at 415 nm [15]. There are no other data in the literature concerning the spectrum of Mo(V) in chloride ionic media.

Based on the assignment given by Aleksandrov et al. [13] Mo(III) dissolved in LiCl–KCl melt can be oxidized to Mo(V) by reaction with Cl_2. The spectrum obtained after 5 min of reaction has been superimposed in Fig. 1

(dashed profile C), and shows that the presence of $MoCl_6^-$ can account for the absorbance below 480 nm, the region of the main difference between spectra A and B, and this thus represents the molybdenum species sublimed under vacuum.

The reaction of the greenish-yellow melt, containing $MoCl_6^-$, with Mo metal resulted in the melt regaining its deep red color. To achieve this the melt was agitated either by shaking the cell or by sparging its entire contents with a flow of gas; Mo particles lifted from the bottom of the cell reacted with Mo(V) to form Mo(III), by shifting the equilibrium (6) to the left.

When chlorine was bubbled in at the bottom of the cell, to agitate the Mo powder, the system behaved differently, Fig. 3. The absorbance at ≈550 nm initially decreased slightly, line B, and after 4 min the maximum was changed to a shoulder, C, that had almost disappeared after two more minutes of chlorine bubbling, D. At the same time the absorbance below 500 nm started to increase, E, and the low energy edge of this very intense band shifted to ≈580 nm. During this time the melt remained deep-red, indicating the presence of a considerable concentration of Mo(III), maintained by the continued oxidation of Mo metal to Mo(III) and (V).

During the experiments in the high temperature melts a very dark product had condensed in the top cold part of the optical cell and in the outlet tube. This is identified as molybdenum pentachloride, formed as a result of the disproportionation of $MoCl_6^{3-}$ [13,14], Eq. (6). The final quenched melts were dark red.

The reaction of Mo metal with Cl_2 in the NaCl–CsCl melt at 550 °C was essentially the same as that described above for the LiCl–KCl melt, except that this time the reaction proceeded faster, by a factor of around two, than in LiCl–KCl melt at 400 °C.

The reaction of molybdenum metal with chlorine in chloride melts proceeds in several stages. The process
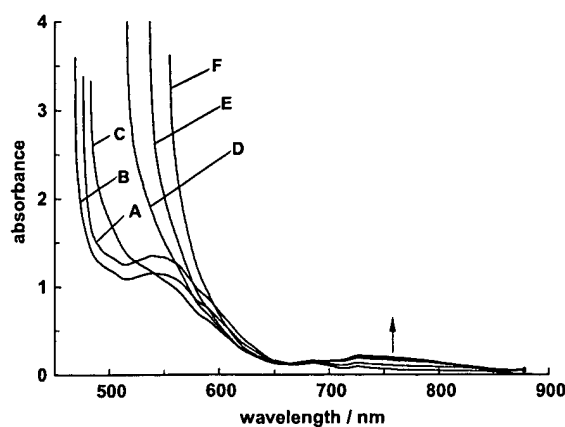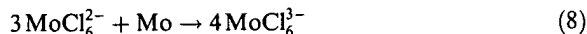

Fig. 3. Reaction of $MoCl_6^{3-}$ and Mo with Cl_2 in LiCl–KCl (400 °C). Time of reaction, min: A, 0; B, 1; C, 4; D, 6; E, 8 and F, 11.

begins from the oxidation of Mo to $MoCl_6^{2-}$, which can disproportionate to Mo(III) and Mo(V) or, in the melts with an abundance of molybdenum, react with Mo to form Mo(III):

$$3\,MoCl_6^{2-} + Mo \rightarrow 4\,MoCl_6^{3-} \qquad (8)$$

Depending on the relative availability of molybdenum and chlorine in the system, the process then leads to the formation of a mixture of Mo(III) and Mo(V) in the melt. Most of Mo(V) can be removed from the melt under vacuum, but even in the absence of chlorine, Mo(V) is constantly formed as a product of the disproportionation of $MoCl_6^{3-}$. The disproportionation reaction can be reversed by stirring or agitating a melt containing an excess of molybdenum metal.

3.2. Reaction of molybdenum with hydrogen chloride

The reaction of powdered molybdenum metal with hydrogen chloride was slower than with chlorine. The spectra obtained in NaCl–CsCl and NaCl–KCl melts at 600 and 700 °C, respectively, are shown in Fig. 4. After 1.5 h in NaCl–CsCl melt, the final concentration of molybdenum was only 0.57 wt%, and that at 700 °C in the NaCl–KCl melt after 0.5 h was 0.30 wt%. Molybdenum(III) was the only oxidation state identified in the melt. Unlike with chlorine, there was no evidence for the formation of Mo(IV) at the early stages of the reaction, thus:

$$Mo + 3\,HCl + 3\,Cl^- \rightarrow MoCl_6^{3-} + 3/2\,H_2 \qquad (9)$$

This reaction is common with other metals in chloride melts, including vanadium [22], uranium [23] and rhenium [2].

3.3. Reaction of molybdenum oxides with chlorine

A series of experiments was performed with molybdenum oxides and chlorine gas. Since molybdenum dioxide is the major molybdenum oxide in irradiated fuel, this study has focused mainly on the behavior of MoO_2.

The reaction of MoO_2 with Cl_2 in LiCl–KCl eutectic melt at 400 °C was slow and resulted in the formation of a pale yellow melt. A considerable amount of a light yellow solid also sublimed from the melt during the reaction and condensed in the cooler top of the cell.

At 700 °C, in NaCl–KCl melt, this reaction was much faster. Fig. 5 shows examples of the spectra recorded. When chlorine was introduced into the cell, the absorbance below 400 nm increased and a peak appeared at ≈350 nm (A, Fig. 5). Bubbling chlorine through the melt quickly produced a yellow solution (spectra B and C in Fig. 5). Spectra of this solution contain the edge of a very intense charge-transfer band below 420 nm and a pronounced shoulder around 490 nm. This profile corresponds to the spectrum of low concentration solutions of $MoOCl_5^{2-}$ [24].

Throughout the experiment there was the continuous sublimation of a light yellow solid on to the top colder part of the cell, similar to that observed in the LiCl–KCl melt. When this solid was exposed to ambient air, its color changed through green to blue in a few minutes.
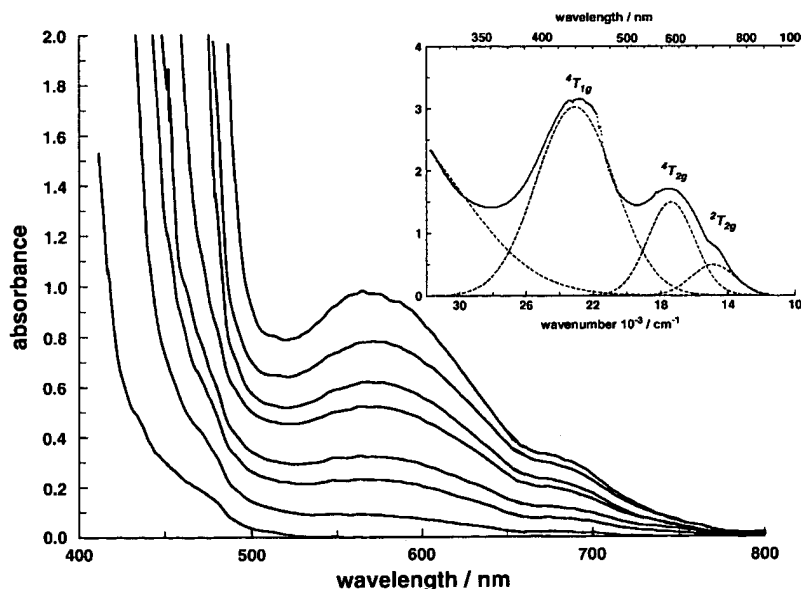

Fig. 4. Spectra recorded at ≈6 min intervals during the reaction of Mo metal with HCl in NaCl–CsCl melt at 600 °C. Final spectrum, and no further reaction, after 45 min. Insert shows spectrum of $MoCl_6^{3-}$ from the reaction of Mo metal with HCl (6 min) in NaCl–KCl melt at 700 °C resolved into individual bands. Transitions from the ground $^4A_{2g}(F)$ state are indicated for the individual bands.
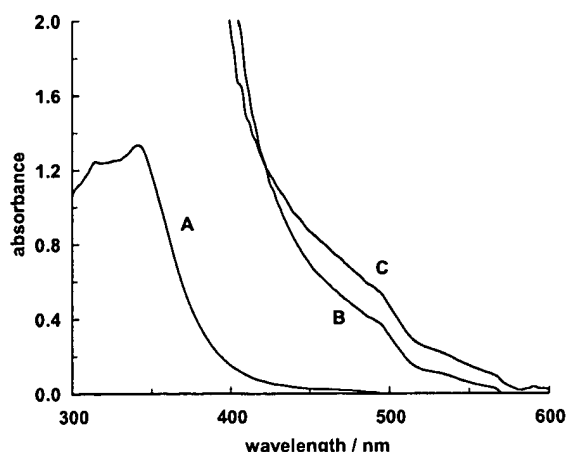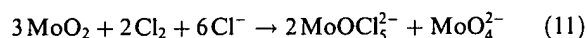
Fig. 5. Reaction of MoO_2 with Cl_2 in NaCl–KCl melt at 700 °C. A, MoO_2 in NaCl–KCl melt for 3 min under Ar atmosphere containing trace amounts of chlorine. B, 3 min chlorination. C, total of 44 min chlorination.

Samples of the yellow solid were therefore carefully collected and stored in a dry box prior to analysis by X-ray powder diffraction and infrared spectroscopy.

The reactions of MoO_2 with Cl_2 proceed as follows:

$$MoO_2 + Cl_2 \rightarrow MoO_2Cl_2 \uparrow \qquad (10)$$

$$3\,MoO_2 + 2\,Cl_2 + 6\,Cl^- \rightarrow 2\,MoOCl_5^{2-} + MoO_4^{2-} \qquad (11)$$

It is possible that some MoO_2Cl_2 also stayed in the melt (as $MoO_2Cl_4^{2-}$) but, unfortunately, in the literature there is no information concerning its electronic spectra. Some oxidation of $MoOCl_5^{2-}$ could also have taken place:

$$MoOCl_5^{2-} + 1/2\,Cl_2 \rightarrow MoOCl_5^- + Cl^- \qquad (12)$$
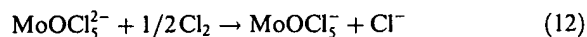
Finally, experiments with molybdenum trioxide, MoO_3, were carried out in a LiCl–KCl eutectic melt at 600 °C. Molybdenum trioxide was soluble in LiCl–KCl melt, and formed a yellow solution and did not need the introduction of chlorine above or into the system before reacting. The initial nature of this solution is uncertain, and it was unstable in that after a few minutes a yellow solid started to condense in the top cool part of the cell, and the yellow solution became paler. This solid is molybdenum oxychloride, MoO_2Cl_2, identified from its infrared spectrum (see below). The other product, which remained in solution, was thus the molybdate ion, MoO_4^{2-}, though it is possible that it could later polymerize. Chlorine bubbling through the melt is not expected to react with molybdate and thus did not change its yellow color; the final spectra consisted only of the low energy edge of charge transfer bands below 400 nm. The chlorine merely swept out the volatile oxychloride.

Thus the reaction of MoO_2 with chlorine in LiCl–KCl and in NaCl–KCl melts results in the formation of the volatile molybdenum oxychloride MoO_2Cl_2 and the pentachloromolybdenyl(V) species, $MoOCl_5^{2-}$. When using MoO_3, MoO_2Cl_2 and molybdate are formed in the *absence* of chlorine, and when it is introduced it sparges out the yellow volatile MoO_2Cl_2.

3.3.1. X-ray diffraction data for MoO_2Cl_2

This yellow volatile compound can in theory be a molybdenum chloride, oxychloride or oxide, of which there are several. Its X-ray diffraction pattern gave for $d(\text{Å})$: 5.54_x, 3.41_6, 3.61_5, 3.47_4, 2.80_3, 4.59_2 and 2.29_2 (subscripts indicate the relative intensity of the peaks, with x identifying the most intense peak). This pattern does not correspond to any of the following molybdenum compounds: $MoCl_5$, $MoCl_4$, $MoCl_3$, $MoCl_2$, $MoOCl_3$, $MoOCl_2$, MoO_2Cl and molybdenum oxides [25], nor their mixture, (and not all of them are yellow in color). Green $MoOCl_4$ is not a candidate, as it decomposes to $MoOCl_3$ and Cl_2 at room temperature. By default, this diffraction pattern is thus that of MoO_2Cl_2. Further reasoning is now given.

From the remaining possible molybdenum species of the oxychloride class, MoO_2Cl_2 is the prime candidate. The formation of molybdenum oxychloride, MoO_2Cl_2, during the chlorination of molybdenum dioxide is well known [26], and this compound is yellow in color [26–29]. The formation of this same molybdenum oxychloride has also been reported [30] upon reaction of sodium chloride with molybdenum trioxide at 400–700 °C (in air):

$$2\,NaCl + 2\,MoO_3 \rightarrow MoO_2Cl_2 + Na_2MoO_4 \qquad (13)$$
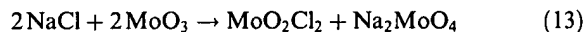
Importantly, yellow MoO_2Cl_2 has been reported as readily reduced and hydrolysed in open air to form a blue compound [31].

The infrared spectrum of the yellow sublimed solid contains bands at 996 cm^{-1} and 968–970 cm^{-1} (due to symmetric and asymmetric $Mo=O$ stretching vibrations, respectively) and at 429–434 cm^{-1} and 451–470 cm^{-1} (symmetric and asymmetric Mo–Cl stretching). The spectrum recorded hereby corresponds to the reported infrared spectra of MoO_2Cl_2 [31–34].

The above X-ray diffraction data can thus be reliably attributed to the molybdenum oxychloride MoO_2Cl_2, and this is, as far as we can find, the first report of its X-ray diffraction pattern.

4. Conclusions

The chlorination of molybdenum metal and oxides in molten chlorides at high temperature was investigated using in situ electronic absorption spectroscopy. The melts investigated were LiCl–KCl eutectic, NaCl–CsCl eutectic and the NaCl–KCl mixture and experiments were performed at various temperatures between 400 and 700 °C.

Molybdenum readily reacts with chlorine and the first detected product of the reaction was the soluble Mo(IV) species, $MoCl_6^{2-}$. Continued reaction yields a mixture of Mo(III) and (V) chlorocomplexes, the ratio of the components depending on the availability of chlorine and molybdenum in the system, and on the efficiency of agitation of the melt. Small amounts of Mo(V) chloride also exit the melt as volatile $MoCl_5$. Essentially all Mo(V) chloride can be removed from the melt under vacuum, or can be reduced to Mo(III) by reacting with Mo metal. The reaction of Mo with hydrogen chloride is much slower than with Cl_2 and results in the formation of only Mo(III) species, $MoCl_6^{3-}$.

Molybdenum dioxide reacts with chlorine, yielding Mo(IV) chloride (which remains in the melt as $MoOCl_5^{2-}$) and volatile molybdenum oxychloride MoO_2Cl_2 (most of which sublimes from the melt). Molybdenum trioxide is soluble in molten chlorides but then decomposes to molybdate and oxychloride. Upon bubbling with chlorine, up to half the molybdenum (the maximum possible) was lost from the melt as volatile MoO_2Cl_2.

Pyrochemical reprocessing of molybdenum using a molten chloride melt and chlorine is thus possible: using HCl gas is less efficient. The reactions were fastest in the NaCl–KCl mixture and this is thus recommended. Both the metal and its oxides can ultimately be converted into a combination of molybdenum chlorocomplexes. The volatiles, mainly $MoCl_5$ and MoO_2Cl_2, can be recovered by sparging or under vacuum.

The X-ray diffaction pattern for MoO_2Cl_2 is reported for the first time.

Acknowledgements

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